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(54) Hydrocarbon compositions containing polyolefin graft polymers.

(57) Polymers having useful properties as oil additives are obtained by incorporating additional functional monomer units into oil-soluble backbone polymers having linear carbon chains, especially ethylene-propylene copolymers and ethylene-propylene-diene terpolymers.

The first functional monomers have at least one nitrogen, sulpher and/or oxygen atom in a heterocyclic ring, preferably phenothiazine or the reaction product of phenothiazine and allyl glycidyl ether.

Optionally a second amine polymer (preferably N-vinylpyrrolidone) can be grafted on to the backbone polymer.

The polymers of the invention constitute dispersant, anti-oxidant, viscosity index improvers for lubricating oils, while the polymers containing both types of monomer unit are also useful as dispersant additives for fuel oils.

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HYDROCARBON COMPOSITIONS CONTAINING POLYOLEFIN GRAFT POLYMERS

This invention relates to hydrocarbons including hydrocarbon fuel oils and lubricating oil. More particularly, it relates to hydrocarbons which contain graft polymers which permit attainment of improved properties.

As is well known to those skilled in the art, hydrocarbon fuels and lubricating oils must be formulated, as by addition of various additives, to improve their properties.

In the case of hydrocarbon fuels, typified by fuels boiling in the gasoline boiling range, kerosene, middle distillate fuels, home heating oils, etc., it is found that after extended periods of storage, they are characterized by undesirable characteristics typified by formation of solid deposits within the system.

In the case of lubricating oils, typified by those employed in railway, automotive, aircraft, marine etc., service, it is found that they become degraded during use, due inter alia to formation of sludge which may be generated by deterioration of the oil or by introduction of undesirable components from other sources including the fuel or the combustion air. In order to maintain and improve the properties of the lubricating oil, various additives have heretofore been provided; and these have been intended to improve the viscosity index, dispersancy, oxidative stability, etc. It is an object of this invention to provide an additive system which permits attainment of improved hydrocarbons. Other objects will be apparent to those skilled in the art.

This invention provides a polymer comprising an oil-soluble backbone polymer having a linear carbon chain attached to which are additional units derived from a first functional monomer having at least one atom of

nitrogen, sulphur and/or oxygen in a heterocyclic ring.

This invention also provides a method of producing such a polymer by heating the backbone polymer and the first functional monomer with a free-radical initiator at a temperature at least as high as the decomposition temperature of the initiator.

In another embodiment, this invention comprises a polymer as defined above and having additional graft units derived from a second monomer which is an amine having a polymerisable ethylene double bond.

This invention also provides methods of producing the polymers having units derived from the second monomer, by:

(i) heating the backbone polymer and the second monomer with a free-radical initiator at a temperature at least as high as the decomposition temperature of the initiator, and subsequently heating the resulting graft polymer with the first functional monomer and the initiator at a temperature at least as high as the decomposition temperature of the initiator, or

(ii) heating the backbone polymer with the first functional monomer, the second monomer and a free-radical initiator at a temperature at least as high as the decomposition temperature of the initiator.

This invention additionally provides a lubricating oil composition containing as additive a polymer of the types defined above.

Moreover, this invention provides a fuel oil composition containing as additive a polymer of the type comprising both types of monomer.

The charge polymer which may be employed according to this invention is an oil-soluble, substantially linear, carbon-carbon backbone polymer. Typical carbon-carbon backbone polymers prepared from monomers bearing an

ethylenically unsaturated polymerizable double bond which may be employed include homopolymers or copolymers prepared from monomers containing moieties of the skeleton

$$\underset{\displaystyle A}{\overset{\displaystyle C{=}C}{|}} \quad \text{and/or} \quad \underset{\displaystyle A}{\overset{\displaystyle C{=}C}{|}}{-}R''{-}C{=}C$$

wherein A may be hydrogen; monovalent hydrocarbon such as alkyl, aryl, etc.; phenyl; acyoxy, such as acetyloxy (or less preferably -COOR where R is hydrocarbon); halide, etc.; R" may be divalent hydrocarbon typified by alkylene, alkarylene, aralkylene, cycloalkylene, arylene, etc.

Illustrative of such monomers may be acrylates, methacrylates, vinyl halides (such as vinyl chloride), styrene, olefins such as propylene, butylene, etc., vinyl acetate; dienes such as butadiene, isoprene, hexadiene, ethylidene norbornene, etc. The polymers can be homopolymers of olefins, (such as polypropylene, polybutylene, etc.) or dienes, (such as hydrogenated polyisoprene), or copolymers of ethylene with e.g. butylene and higher olefins, styrene with isoprene and/or butadiene may be employed. The preferred carbon-carbon backbone polymers include ethylene-propylene copolymers (EPM or EPR) and ethylene-propylene-diene terpolymers (EPDM or EPT).

When the charge polymer is an ethylene-propylene copolymer (EPM, also called EPR polymers), it may be formed by copolymerization of ethylene and propylene under known conditions, preferably Ziegler-Natta reaction conditions. The preferred EPM copolymers contain units derived from ethylene in amounts of 40 to 70 mol %, preferably 50 to 60 mol %, e.g. 55 mol %, the remainder being derived from propylene.

The molecular weight M_n of the EPM copolymers which may be employed may be 10,000 to 1,000,000, preferably 20,000 to 200,000, e.g. 140,000. The molecular weight distribution may be characterized by $\bar{M}_w/\bar{M}_n$ of less than 15, preferably 1.2 to 10, e.g. 1.6.

Illustrative EPM copolymers which may be employed in this invention are the following, the first listed being preferred:

A. Epsyn brand of EPM, marketed by Copolymer Rubber and Chemical Corporation, containing 60 mol % of units derived from ethylene and 40 mol % of units derived from propylene, having a molecular weight $\bar{M}_n$ of 140,000 and a $\bar{M}_w/\bar{M}_n$ (polydispersity index) of 1.6.

B. The Epcar 505 brand of EPM, marketed by B.F. Goodrich Co., containing 50 mol % of units derived from ethylene and 50 mol % of units derived from propylene, and having a $\bar{M}_n$ of 25,000 and a polydisparity index of 2.5.

C. The Esprene brand of EPR, marketed by Sumitomo Chemical Co., containing 55 mol % of units derived from ethylene and 45 mol % of units derived from propylene and having a $\bar{M}_n$ of 25,000 and polydispersity index of 2.5.

When the charge polymer is an ethylene-propylene-diene terpolymer (EPT or EPDM), the third monomer is commonly a non-conjugated diene typified by dicyclopentadiene; 1,4-hexadiene; or ethylidene norbornene. Polymerization is effected under known conditions generally comparable to those employed in preparing the EPM products. The preferred terpolymers contain units derived from ethylene in amount of 40 to 70 mol %, preferably 50 to 65 mol %, e.g. 60 mol %, and units derived from the propylene in amount of 20 to 60 mol %, preferably 30 to 50 mol %, e.g. 38 mol %, and units derived from third diene monomer in amount of 0.5 to 15 mol %, preferably 1 to 10 mol %, say 2 mol %. The molecular weight $\bar{M}_n$ of the terpolymers may typically be 10,000 to 1,000,000, preferably 20,000 to 200,000, e.g. 120,000. Molecular weight distribution of the useful polymers is preferably narrow, viz a $\bar{M}_w/\bar{M}_n$ of typically less than 15, preferably 1.5 to 10, e.g. 2.2.

Illustrative EPT terpolymers which may be employed in this invention are set forth below, the first listed being preferred:

A. Epsyn 4006, marketed by Copolymer Rubber and Chemical Corp., containing 58 mol % of units derived from ethylene, 40 mol % of units derived from propylene, and 2 mol % of units derived from ethylidene norbornene and having a $\bar{M}_n$ of 120,000 and a polydispersity index $\bar{M}_w/\bar{M}_n$ of 2.2.

B. Ortholeum 5655, marketed by DuPont, containing 62 mol % of units derived from ethylene, 36 mol % of units derived from propylene, and 2 mol % of units derived from 1,4-hexadiene, and having a $\bar{M}_n$ of 75,000 and a polydispersity index $\bar{M}_w/\bar{M}_n$ of 2.

C. Ortholeum 2052, marketed by DuPont, containing 62 mol % of units derived from ethylene, 36 mol % of units derived from propylene, and 2 mol % of units derived from 1,4-hexadiene and having a $\bar{M}_n$ of 35,000 and a polydispersity $\bar{M}_w/\bar{M}_n$ of 2.

D. Royalene marketed by Uniroyal containing 60 mol % of units derived from ethylene, 37 mol % of units derived from propylene, and 3 mol % of units derived from dicyclopentadiene and having a $\bar{M}_n$ of 100,000 and a polydispersity index $\bar{M}_w/\bar{M}_n$ of 2.5.

E. Epsyn 40A, marketed by Copolymer Rubber and Chemical Corp., containing 60 mol % of units derived from ethylene, 37 mol % of units derived from propylene, and 3 mol % of units derived from ethylidene norbornene and having a $\bar{M}_n$ of 140,000 and a polydispersity index $\bar{M}_w/\bar{M}_n$ of 2.

The EPM and EPT polymers may contain minor portions (typically less than 30%) of units derived from other copolymerizable monomers.

In the process of this invention, units derived from the first functional monomer are bonded onto these oil-soluble, substantially linear, carbon-carbon, backbone polymers. When the first functional monomer includes a polymerizable ethylenic double bond, (as is the case for example with the reaction product of allyl glycidyl ether and phenothiazine) bonding may be effected by graft

polymerization under graft polymerization conditions.

When the functional monomer does not contain such a polymerizable ethylenic double bond (as is the case for example, with the preferred phenothiazine), then bonding may be effected in the presence of a free-radical initiator catalyst.

It is believed that the best anti-oxidant activity in the desired polymer product is attained by bonding heterocyclic compounds which exhibit anti-oxidant activity when present in unbonded form. Preferred of these latter is phenothiazine.

The functional monomers which may be employed may be monocyclic, or polycyclic; and the nitrogen, sulphur and/or oxygen may be contained in the same or a different ring. In the preferred embodiment, the functional monomer is polycyclic and nitrogen and sulphur are in the same heterocyclic ring.

The functional monomer can be a heterocyclic/aromatic or heterocyclic compound containing sulphur, nitrogen or oxygen, or a combination thereof. The compounds which may be used as the functional monomer include:

1) phenothiazine and C-substituted and/or N-substituted phenothiazines. Substituents may include hydrocarbon groups, such as alkyl, alkenyl, cycloalkyl, aryl or alkaryl, or heterocyclic groups, including oxygen, nitrogen, sulphur, halide or combinations thereof. Typically, the C-substituted phenothiazine may include alkyl or alkenyl phenothiazines, alkoxy phenothiazines, hydroxyalkyl phenothiazines, aminophenothiazines, nitrophenothiazines, 3-formyl-10-alkyl-phenothiazine, 2-amino-4-(2-phenthiazinyl) thiazole, alpha (2-phenothiazinyl) thioacetomorpholide, etc. Typical N-substituted phenothiazines include N-vinyl phenothiazine, N-acrylamidomethyl phenothiazine, beta-(N-phenothiazinyl) ethyl

vinyl ether, beta-(N-phenothiazinyl) ethyl methacrylate, reaction products of allyl glycidyl ether or glycidyl methacrylate with phenothiazine; etc.

2) imidazoles or benzimidazoles, such as 2-mercaptobenzimidazole, 2-mercapto toluimidazole or 2-mercapto-1-urethyl imidazole; etc.

3) thiazoles or benzothiazoles, such as 4-methyl-5-vinylthiazole, 2-amino-4-methylthiazole, 2-mercapto-4-phenylthiazole, 2-mercaptobenzothiazole; etc.

4) triazoles and benzotriazoles, such as 3-mercapto-1H-1,2,4-trizole, 3-amino-5-methylthio-1H-1,2,4-triazole; etc.

5) thiadiazoles, benzothiadiazoles, thiazolines and benzothiazolines, or thiazolidines, such as 2-mercapto-thiazoline, 1,2,5-thiadiazoline; etc.

6) pyrimidines, such as 2-amino-4-methylpyrimidine, 2-mercaptopyrimidine; etc.

7) pyridines, such as 2-mercaptopyridine, 4-mercapto-pyridine, 2-mercaptopyridine-N-oxide; etc.

8) piperidines and pyrrolidinones;

9) oxazoles and benzoxazoles, such as 2-mercaptobenzoxazole; etc.

10) mercaptophenols, thiomorpholine, 6-mercaptopurine, and 2-thiophenemethylamine.

The preferred first functional monomer is phenothiazine, which is a three-ring compound containing nitrogen and sulphur atoms in the same ring. It is preferred to use one functional monomer although it may be possible to use more than one such functional monomer, i.e. to bond them to the polymer either simultaneously or sequentially.

In the process of this invention producing the above-described polymers, 100 parts by weight of charge

EPM or EPT may be added to 100 to 1000 parts by weight, e.g. 300 parts by weight of diluent-solvent. Typical diluent-solvents are hydrocarbon solvents, such as n-hexane or n-heptane, tetrahydrofuran, or mineral oil. A preferred solvent is a commercial hexane containing principally hexane isomers. The reaction mixture may then be heated to a temperature of 60 to 180°C, preferably 150 to 170°C, e.g. 155°C at a pressure of 0.2 to 2.2 MPa, preferably 1.3 to 1.65 MPa, e.g. 1.5 MPa.

The first functional monomer, typically phenothiazine, is admitted in amount of 1 to 40 parts by weight, e.g. 2 parts by weight, as a solution in 2 to 20 parts by weight, e.g. 8 parts by weight of diluent-solvent, typically tetrahydrofuran (THF). There is also added a solution in hydrocarbon of a free radical initiator. Typical free radical initiators include dicumyl peroxide, di-t-butyl peroxide, benzoyl peroxide, di-isopropyl peroxide, azobisisobutyronitrile, etc. The solvent is preferably the same as that in which the EPM or EPT is dissolved. The initiator may be added in an amount of 0.2 to 40 parts by weight, e.g. 1 part by weight in 0.8 to 120 parts by weight, e.g. 3 parts by weight of solvent (e.g. hexane).

The reaction is carried out at a temperature at least as high as the decomposition temperature of the initiator, typically 60°C or higher.

Reaction is typically carried out at 60 to 180°C, e.g. 155°C and 1.3 to 1.65 MPa, e.g. 1.5 MPa, during which time bonding of the functional monomer onto the base EPM or EPT polymer occurs.

Typically the product contains 0.1 to 60 units, e.g. 3 units, derived from functional monomer per 1000 carbon atoms of the charge backbone polymer.

For ease of handling, the polymerization solvent may be exchanged with a heavier solvent, such as SUS 100 oil typified by SNO-100. Product polymer is typically obtained as a solution of 4 to 20 parts by weight, e.g. 8.5 parts by weight thereof in 80 to 96 parts by weight,

e.g. 91.5 parts by weight of solvent.

In another embodiment of this invention, graft units derived from a second amine graft monomer are grafted on.

The second monomer which may be grafted onto the backbone polymer according to one embodiment of this invention may have the formula

$$R - \underset{}{\overset{R''}{\overset{|}{N}}} - R'$$

wherein R is a hydrocarbon group having a polymerizable ethylenic double bond, and R' and R", which may be the same or different, are each hydrogen, a hydrocarbon group, or a hydrocarbon group with an oxygen, sulphur or nitrogen atom, or R' and R" together with the nitrogen atom to which they are attached constitute a heterocyclic ring. R may for example be an alkenyl or cycloalkenyl group (including such groups bearing inert substituents) e.g. vinyl, allyl, $C{=}C{-}C_6H_4{-}$, etc. and R' and R" may be hydrogen or a hydrocarbon including alkyl, alkaryl, aralkyl, cycloalkyl, and aryl. The group -NR'R" may represent a heterocyclic ring as in the preferred N-vinyl pyrrolidone; 1-vinyl imidazole; or 4-vinyl pyridine. R' and R" may be a hydrogen or a hydrocarbon moiety containing one or more nitrogen, sulphur or oxygen atoms. Illustrative amines which may be employed include N-vinylpyrrolidone, 1-vinylimidazole, 4-vinylpyridine, and allylamine; N-vinylpyrrolidone being preferred.

The second monomer may alternatively be a more complex amine reaction product, formed by the reaction of an amine, typified by morpholine or N-methyl piperazine, and an epoxy compound typified by allyl glycidyl ether. It may be a monomer formed for example from the reaction of crotonaldehyde and N-(3-aminopropyl) morpholine.

The temperatures, pressures, solvents, initiators, etc. used to graft on the second monomer may be generally the same as those used to add the first monomer to the backbone polymer, and so will not be repeated here.

In this embodiment of the invention, the second (amine) monomer is preferably grafted on to the backbone polymer before the first monomer.

In the preferred two step process, the second monomer, typically N-vinyl-pyrrolidone, in an amount of 1 to 40 parts by weight, e.g. 5 parts by weight, and a hydrocarbon solution of the initiator are added to a solution of the backbone polymer, preferably in the same solvent. The initiator may be added in an amount of 0.2 to 10 parts by weight, e.g. 2 parts by weight in 0.8 to 40 parts by weight, e.g. 16 parts by weight of solvent.

The reaction is carried out at a temperature at least as high as the decomposition temperature of the initiator, typically 60°C or higher.

Reaction is typically carried out at 60 to 180°C, e.g. 155°C, and 1.3 to 1.65 MPa, e.g. 1.5 MPa during which time graft polymerization of the amine onto the backbone polymer occurs. The final product graft polymer may be typically characterized by the presence of the following typical units:

$$
\begin{array}{cccc}
 & \mathrm{C} & & \\
 & | & & \\
- & \mathrm{C} & -(\mathrm{CH_2} - & \mathrm{CH})_n- \\
 & | & & | \\
 & \mathrm{C} & & \mathrm{R'''}\text{-}\mathrm{NR'R''}
\end{array}
$$

in which n is at least 1. Typically there may be 0.1 to 80, e.g. 6 amine units per 1000 carbon atoms in the polymer backbone. R"' is a saturated divalent group corresponding to the group R in the amine monomer.

In this embodiment of the invention, the first monomer is subsequently reacted with the resulting polymer having grafted amine units. Although it may be possible to effect bonding and graft polymerization simultaneously, it is preferred to effect graft polymerization first and thereafter bonding. It is not possible to incorporate the first monomer before the second.

The first monomer has already been fully defined above, and is incorporated in the same way as before.

The first monomer, typically phenothiazine, is admitted in an amount of 1 to 40 parts by weight, e.g. 4 parts by weight, as a solution in 1 to 40 parts by weight, e.g. 16 parts by weight, of diluent-solvent-typically tetrahydrofuran (THF). This is followed by a hydrocarbon solution of initiator. The preferred amount in this embodiment is 0.2 to 40 parts by weight, e.g. 2 parts by weight of initiator in 0.8 to 40 parts by weight, e.g. 6 parts by weight of solvent hexane. Temperature and pressure conditions are generally in the same ranges as already defined.

For ease of handling, the polymerization solvent may be exchanged with a heavier solvent, such as SUS 100 oil. Product graft polymer is typically obtained as a solution of 4 to 20 parts by weight, e.g. 8.5 parts by weight thereof in 80 to 96 parts by weight, e.g. 91.5 parts by weight of solvent.

Although it is preferred to graft the second monomer onto the base polymer and thereafter to bond the first monomer onto the so formed graft polymer, it is possible to effect simultaneous reaction of first and second monomers, but not to incorporate the first monomer before the second.

The product so formed in this embodiment of the invention may be an oil-soluble, substantially linear, carbon-carbon backbone polymer of molecular weight $\bar{M}_n$ of 10,000 to 1,000,000, preferably 20,000 to 200,000, e.g. 140,000, bearing thereon (per 1,000 carbon atoms in the polymer backbone) 0.1 to 80 units, preferably 1 to 15 units, e.g. 6 units of second graft monomer, and 0.1 to 60 units, preferably 1 to 12 units, e.g. 3 units of first monomer.

The polymers prepared with both types of monomer may find use in middle distillate fuel oils as dispersants when present in effective amount of 0.001 to 2 weight %, e.g. 0.5 weight %. Typical fuel oils may include middle distillate fuel oils including kerosene, home heating oils, diesel fuel, etc.

The polymer prepared from either embodiment may find use in lubricating oils as multifunctional additives (e.g. dispersant, viscosity index improvers which provide anti-oxidant properties, etc.) when present in effective amount of 0.2 to 5 weight %, preferably 0.4 to 3 weight %, e.g. 0.9 weight %.

Lubricating oils in which the dispersant viscosity index improvers of this invention may find use may include automotive, aircraft, marine, railway, etc. oils; oils used in spark ignition or compression ignition; summer or winter oils; etc. Typically the lubricating oils may be characterized by an initial boiling point (ibp) of 300 to 350°C, e.g. 320°C, an end point (ep) of 400 to 650°C, e.g. 555°C, and a density of 0.870 to 0.905 g/cm^3, e.g. 0.882 g/cm^3.

A typical lubricating oil in which the polymer of this invention may be present may be a standard SAE 5W-30 hydrocarbon motor oil formulation having the following composition:

	weight %
Base Oil	82
-Viscosity Index Improver (10 weight % of ethylene-propylene copolymer in 90 weight % inert oil)	9
-Standard Additive Package Polyisobutenyl ($\bar{M}_n$ 1290) succinimide (dispersant); calcium sulfonate (detergent); zinc dithiophosphate (anti-wear); di-nonyl diphenyl amine (anti-oxidant); 4,4'-methylene-bis(2,6-di-t-butyl phenol) (anti-oxidant).	9

Use of the additive of this invention makes it possible readily to increase the viscosity index by 25 to 40 units, e.g. 35 units and to obtain improved ratings on the tests measuring the dispersancy of the system. The viscosity index is determined by ASTM Test D-445.

The novel polymers are also characterized as anti-oxidants as determined by the Bench Oxidation Test. In

this test, a solution (8.5 weight %) of test polymer in SNO-100 oil is diluted with SNO-130 to give a 1.5 weight % solution of the test polymer. The solution is heated with stirring and air agitation. Samples are withdrawn periodically for analysis by Differential Infrared Absorption (DIR) to observe changes in the intensity of the carbonyl vibration band at 1710 cm^{-1}. Higher carbonyl vibration band intensity indicates a lower thermal-oxidative stability of the sample.

Dispersancy is determined by the Bench VC Test (BVCT). In this test, the turbidity of an oil containing an additive is measured after heating the test oil to which has been added a standard blow-by. The result correlates with dispersancy is compared to three reference standards (Excellent, Good, and Fair) tested simultaneously with the test sample. The numerical rating decreases with an increase in dispersant effectiveness. Results similar to or lower than that of the Good reference indicate that the additive is a good dispersant.

It appears that the second graft monomer (i.e. the amine) used in practice of this invention provides improved dispersant properties to the base polymer (which provides viscosity index improvement); and the first functional monomer provides improved anti-oxidant properties. Thus it is possible to obtain product polymers which serve as multifunctional additives (dispersants, anti-oxidants, viscosity index improvers) when added to a hydrocarbon lubricating oil or to a synthetic type lubricating oil.

The so-prepared graft polymers may find use in lubricating oils as dispersant anti-oxidant, viscosity index improvers when present in effective amount of 0.2 to 5 weight %, preferably 0.4 to 3 weight %, e.g. 0.9 weight %.

The novel polymers may also be characterized as deposit protection agents as measured by the Single Cylinder CEC MWM-B Diesel Engine Test (DIN 51361 Parts I,

II and IV). In this test, a solution (8.5 weight %) of polymer in SNO-100 oil is blended into a fully formulated oil which does not contain a VI improver. Results are presented in "Merits", a higher merit evidencing better protection against deposits.

The polymer products of this invention may be used in middle distillate fuel oils to permit attainment of improved storage stability as measured by the Potential Deposit Test (PDT) - ASTM Test D-2274.

A rating of 1 or 2 is good; and a rating of 3 or 4 is unsatisfactory.

It is possible by use of the compositions of this invention to improve the PDT rating of a charge diesel fuel from 4+ to a satisfactory rating of 1 by use of only 70 g/m^3 of active ingredient. When used in fuels, the additives may be present in amount of 0.5 to 750 g/m^3, preferably 25 to 300 g/m^3, e.g. 70 g/m^3.

Practice of the process of this invention will be apparent to those skilled in the art from the following Examples wherein, as elsewhere in this specification, all parts and percentages are by weight unless otherwise set forth. Control Examples are designated by an asterisk.

EXAMPLE 1

In this Example, which describes the best mode presently known of carrying out the embodiment using only the first monomer, the charge EPM polymer is the Epsyn polymer of molecular weight $\bar{M}_n$ of 140,000, of $\bar{M}_w/\bar{M}_n$ ratio of 1.6, and containing 60 mol % of units derived from ethylene and 40 mol % of units derived from propylene. 100 parts of this polymer are dissolved in 300 parts of commercial hexane and added to a reaction vessel.

The reaction vessel is purged with nitrogen and heated to 155°C at 1.48 MPa. Phenothiazine (2 parts) dissolved in 8 parts of tetrahydrofuran is added, followed by a solution of 1 part of dicumyl peroxide in 3 parts of commercial hexane. The mixture is stirred at 155°C and 1.48 MPa for 1 hour. Solvent Neutral Oil SNO-100 (SUS 100) (1076 parts) is then added; and the hexane is distilled off at 90 to 120°C. The resulting solution contains about 8.5 % of polymer.

EXAMPLES 2 to 4

The process of Example 1 is carried out using the following charge polymers:

Example 2 : Epsyn 4006.
Example 3 : Ortholeum 2052.
Example 4 : Royalene.

EXAMPLE 5*

In this control Example, 100 parts of the same charge EPM copolymer as used in Example 1 is mixed with 1076 parts of SNO-100 oil at 80 to 90°C and the mixture is agitated under nitrogen for 24 hours. There is then added phenothiazine (2 parts) dissolved in 8 parts of tetrahydrofuran; and the mixture is maintained at 80 to 90°C for one hour.

EXAMPLE 6*

In this control Example, the procedure of Example 5* is followed except that the phenothiazine in tetrahydrofuran is not added.

EXAMPLE 7

In this experimental Example, the procedure of Example 1 is followed except that the polymer is EPDM containing 64 mol % of units derived from ethylene, 35 mol % of units derived from propylene, and 1 mol % of units derived from 1,4-hexadiene and having a $\bar{M}_n$ of 75,000 and a $\bar{M}_w/\bar{M}_n$ of 2.

EXAMPLE 8*

In this control Example, the procedure of Example 6* is followed, except that the polymer employed is the same polymer as employed in Example 7.

EXAMPLE 9

In this experimental Example, the procedure of Example 1 is followed, except that the functional monomer is (instead of phenothiazine) a monomer prepared by heating for one hour at 100 to 120°C, a mixture of equimolar amounts of allyl glycidyl ether and phenothiazine.

The products of Examples 1 and 5 to 9 are subjected to the Bench Oxidation Test (BOT) to determine whether the additive is a satisfactory anti-oxidant. In the test, an 8.5% solution of the test polymer in SNO-100 oil is diluted with SNO-130 oil to give a 1.5% solution of the test polymer. This solution is heated with stirring and air agitation. Samples are withdrawn periodically and analyzed by (i) Differential Infrared Absorption (DIR) to observe changes in the intensity of the carbonyl vibration band at 1710 cm^{-1}, (ii) the Visual Clarity Test and (iii) the Lumetron Turbidity Test.

The Oxidation Index is reported as the Carbonyl Group Absorbance in the Differential Infrared Spectra after

144 hours of oxidation. The Oxidation Index may range from 0 up to 100 and a low rating is desired. The results below 4 are considered excellent.

The clarity of the products of Example 1 and 5 to 9 is also reported visually and by the Lumetron Turbidity Test after 144 hours of oxidation. In the Lumetron Turbidity Test, the turbidity of the product is determined by a Lumetron Photoelectric Colorimeter.

The Lumetron Turbidity is reported on a scale of 0 to 100. A rating of below 20 is satisfactory; higher ratings are less satisfactory.

The product of Example 1 is also subjected to the standard CEC MWM-B Diesel Engine Test (DIN 51361 Parts I, II and IV).

The following Table notes the results - including a series of tests on a typical commercial formulation.

TABLE

		Clarity at 144 hours		
Example	Oxidation Index	Visual	Lumetron Turbidity	MWM-B Merits
Commercial	9.5	Turbid	60	53
1	1.1	Clear	14	67
5*	1.8	Turbid	100	-
6*	15	Turbid	100	-
7	1.3	Clear	12	-
8*	16	Turbid	100	-
9	2.1	Clear	16	-

From the above Table, it is apparent that the experimental Examples 1, 7 and 9 are characterized by a desirably low Oxidation Index (i.e. freedom from oxidation), by a visually clear reading, and by a desirably low Lumetron Turbidity rating. Control Examples 6* and 8*, which fall outside the scope of this invention, are characterized by undesirably higher Oxidation Indices, by a visually turbid reading, and by undesirably high Lumetron Turbidity ratings.

Control Example 5* is unsatisfactory by the latter two criteria.

Experimental Example 1 showed better deposit protection (higher merits in the MWM-B test) than currently-manufactured commercial dispersant olefin copolymer (DOCP) viscosity index improver.

EXAMPLES 10 and 11*

In Example 10, the product of Example 1, containing the functionalized EPM, is tested as a viscosity index improver in a conventional mineral lubricating oil at concentration of 11.5% (corresponding to 1% of grafted EPM); and in control Example 11*, a formulation containing 11.5% of commercial non-dispersant VI improver (corresponding to 1% active ingredient) in the same system is tested.

TABLE

Example	Kinematic Viscosity (cSt) 40°C	Kinematic Viscosity (cSt) 100°C	Thickening Power (TP) @ 100°C	TP/W % Polymer
10	58.2	9.89	5.09	0.65
11*	62.5	10.53	5.60	0.66

Thickening Power (TP) is calculated by subtracting the viscosity of the Base Blend (4.8 cSt @ 100°C) from that of the test specimen measured at 100°C. This number (e.g. 9.89-4.8 or 5.09 in the case of Example 10) is the Thickening Power at 100°C.

EXAMPLE 12

In this Example, which describes the best mode presently known of carrying out the embodiment using both types of monomer, 100 parts of the polymer used in Example 1, dissolved in 300 parts of commercial hexane are added to a reaction vessel. In the first step, the mixture is heated to 155°C with agitation under nitrogen atmosphere at 1.48 MPa. N-vinyl pyrrolidone (5 parts dissolved in 15 parts

of hexane) is added followed by 5 parts of 25% dicumyl peroxide in hexane. The reaction mixture is stirred for one hour.

In the second step, phenothiazine (4 parts) dissolved in 16 parts of tetrahydrofuran is added, followed by a solution of 2 parts of dicumyl peroxide in 6 parts of commercial hexane. The mixture is stirred at 155°C and 1.48 MPa for 1 hour. Solvent Neutral Oil (SUS 100) (1076 parts) is then added; and the hexane is distilled off at 90 to 120°C. The resulting solution contains about 8.5% polymer.

The product polymer contains (per 1000 carbon atoms of polymer backbone) about 6 units derived from N-vinyl pyrrolidone and 3 units derived from phenothiazine.

EXAMPLES 13 to 15

The process of Example 12 is repeated using the respective charge polymers used in Examples 2 to 4.

EXAMPLE 16*

In this control Example, the N-vinylpyrrolidone grafted EPM (as a 25% solution in hexane) is prepared as in Example 12. Solvent hexane is exchanged for SNO-100 oil (1076 parts) to give a solution containing 8.5% of polymer.

There are then added 4 parts of phenothiazine dissolved in 16 parts of tetrahydrofuran; and the mixture is maintained at 70 to 80°C under nitrogen for one hour.

This mixture contains the same quantity of N-vinyl pyrrolidone and of phenothiazine as does the product of Example 12, but in this Example 16*, the phenothiazine is merely admixed.

EXAMPLE 17*

In this control Example, the procedure of Example 16* is followed, except that the phenothiazine in tetrahydrofuran is not added.

EXAMPLE 18

In this experimental Example, the procedure of Example 12 is followed, except that the first graft monomer is (instead of N-vinylpyrrolidone) a monomer (8 parts) prepared by heating, for one hour at 100 to 120°C, a mixture of equimolar amounts of allyl glycidyl ether and morpholine. The polymer product contains (per 1000 carbon atoms in the polymer backbone) 5 units derived from the reaction product of allyl glycidyl ether and morpholine, and 3 units derived from phenothiazine. It is recovered as a 8.5% solution in SNO-100 oil.

EXAMPLE 19*

In this control Example, the procedure of Example 16* is followed, except that the first graft monomer is the reaction product of allyl glycidyl ether and morpholine, prepared as in Example 18.

EXAMPLE 20*

In this control Example, the procedure of Example 17* is followed, except that the first graft monomer is the reaction product of allyl glycidyl ether and morpholine - prepared as in Example 18.

EXAMPLE 21

In this experimental Example, the procedure of Example 12 is followed, except that the first functional monomer is (instead of N-vinyl pyrrolidone) a monomer (6 parts) prepared by heating for one hour at 100 to 120°C, a mixture of equimolar amounts of allyl glycidyl ether and N-methylpiperazine. The polymer product contains (per 1000 carbons of polymeric chain) 4 units derived from the reaction product of allyl glycidyl ether and N-methyl piperazine and 3 units derived from phenothiazine. It is recovered as a 8.5% polymer solution in SNO-100 oil.

EXAMPLE 22

In this experimental Example, the procedure of Example 12 is followed, except that the first functional monomer is (instead of N-vinyl pyrrolidone) a monomer (8 parts) prepared by heating for one hour at 90 to 100°C, a mixture of equimolar amounts of crotonaldehyde and N-(3-aminopropyl)morpholine. The polymer product contains (per 1000 carbons of polymeric chain) 4.5 units derived from the reaction product of crotonaldehyde and N-(3-aminopropyl)morpholine, and 3 units derived from phenothiazine. It is recovered as a 8.5% solution in SNO-100 oil.

EXAMPLE 23

In this experimental Example, 100 parts of the polymer used in Example 1 are dissolved in 300 parts of commercial hexane and added to a reaction vessel. The mixture is heated to 155°C with agitation under nitrogen at 1.48 MPa. There are added (i) 5 parts of N-vinylpyrrolidone, dissolved in 15 parts of hexane, (ii) 2 parts of phenothiazine, dissolved in 8 parts of tetrahydrofuran, and (iii) 6.0 parts of dicumyl peroxide dissolved in 18 parts of hexane.

The mixture is stirred at 155°C and 1.48 MPa for one hour under nitrogen. Solvent Neutral Oil (SUS 100) is then added (1076 parts); and the hexane is distilled off at 90 to 120°C. The resulting solution contains 8.5% polymer.

The product polymer contains (per 1000 carbon atoms in the polymer backbone) about 6 units derived from N-vinyl pyrrolidone and 1.5 units derived from phenothiazine.

Each of the products of Examples 12 and 16* to 23 is formulated with a fully formulated base blend to yield a composition containing 0.85% of polymer; and these compositions are subjected to the Bench VC Test (BVCT).

The fully formulated base blend contains the following components:

Components	Weight %
SNO-130 Oil	75.25
SNO-320 Oil	21.64
Zinc dithiophosphate (anti-wear)	1.12
Naugalube 438 Brand of 4,4'-di-nonyl-di-phenyl amine (anti-oxidant)	0.39
Surchem 521 Brand of Mg Sulfonate (detergent)	1.50
Silicone polymer (anti-foamant)	150 ppm

This oil has the following properties:

Property	Value
Viscosity Kin 40°C cs	31.50
100°C cs	5.36
Pour Point	-15
Ash sulphated % (ASTM D-874)	0.93
Phosphorus % (X-ray)	0.11
Sulphur % (X-ray) total	0.40
Zinc % (X-ray)	0.12
Magnesium %	0.33
Cold Cranking Simulator (cP @ -18°C)	1660

The products of Examples 12 and 16* to 23 are subjected to the Bench Oxidation Test to determine whether the additive is a satisfactory anti-oxidant. They are also tested in the Clarity Test and the Lumetron Turbidity Test.

Example	Oxidation Index	Clarity at 144 hours: Visual	Clarity at 144 hours: Lumetron Turbidity	BVCT	Standards Excellent/Good/Fair
12	1.8	Clear	16	32.1	9.1/31.0/61.0
16*	2.5	Turbid	100	-	
17*	9.5	Turbid	100	36.0	10.1/27.7/51.9
18	2.5	Clear	20	34.8	9.1/31.0/61.0
19*	3.0	Turbid	100	-	
20*	13.0	Turbid	100	38.5	15.8/31.8/64.6
21	1.8	Clear	16	23.1	11.1/25.2/65.3
22	1.7	Clear	14	37.1	13.7/25.8/68.2
23	2.2	Clear	18	36.0	10.2/28.3/52.1

From the above Table, it is apparent that the experimental Examples 12, 18 and 21 to 23 are characterized by a desirably low Oxidation Index (i.e. freedom from oxidation), by a visually clear reading, and by a desirably low Lumetron Turbidity rating. Control Examples 17* and 20*, which fall outside the scope of this invention, are characterized by undesirably higher oxidation indices, by a visually turbid reading, and by undesirably high Lumetron Turbidity rating. Control Examples 16* and 19* are unsatisfactory by the latter two criteria.

Experimental Examples 1, 18 and 21 to 23 are also characterized by satisfactory BVCT ratings.

It is clear from these tests that the products of the instant invention which contain polymers bearing first dispersant graft monomers and second anti-oxidant monomers possess the ability to form lubricating oils characterized by desirable properties including high dispersancy, anti-oxidant activity, and desirable viscosity index.

EXAMPLE 24*

In this control Example, a base diesel fuel having the following properties is tested in the Potential Deposit Test and found to have an unsatisfactory rating of 4+.

Property	Value
Lumetron Turbidity	8
Density (g/cm^3)	0.8606
Colour ASTM	3.0
Kin. Vis. (cSt @ 100°C)	805.5
Flash Point (Cleveland Open Cup) (°C)	100.5
Ash %	0.02

EXAMPLE 25

In this experimental Example, there is added to the base fuel of Example 24*, 8.5% of the polymer of Example 12 to yield a mix containing 0.01% (nitrogen content of 0.054%).

The modified diesel fuel is found to have a PDT rating of 1 which is satisfactory.

EXAMPLE 26*

In this control Example, a commercial olefin copolymer dispersant VI improver is blended into formulated oil not containing a VI improver. The blend is subjected to the single cylinder MWM-B Diesel Engine Test. In this test, results are presented in merits which correlate with amount of deposits. Higher merits correspond to lower deposits.

EXAMPLES 27 and 28

In these experimental Examples, the procedure of Example 26* is followed, except that the product of Example 12 is added in Example 27 and the product of Example 21 is added in Example 28 (instead of the commercial olefin copolymer dispersant VI improver) to a formulated oil not containing a VI improver.

Example	Polymer Product Example	MWM-B Merits
26*	Commercial DOCP VII	53
27	12	64
28	21	63

From the above Table, it is apparent that the experimental Examples 27 and 28 are characterized by a better deposit protection (higher merits) than the commercial dispersant olefin copolymer VI improver of Example 26*.

CLAIMS:

1. A polymer comprising an oil-soluble backbone polymer having a linear carbon backbone and additional units thereon derived from a first functional monomer characterized in that said functional monomer has at least one atom of nitrogen, sulphur and/or oxygen in a heterocyclic ring.

2. A polymer according to claim 1 characterized in that the backbone polymer is an ethylene-propylene copolymer or an ethylene-propylene-diene terpolymer.

3. A polymer according to claim 1 or 2 characterized in that the backbone polymer has a molecular weight $\bar{M}_n$ of 10,000 to 1,000,000.

4. A polymer according to any of claims 1 to 3 characterized in that the first functional monomer comprises a phenothiazine; an imidazole or benzimidazole; a thiazole or benzothiazole; a triazole or benzotriazole; a thiadazole, benzothiadiazole, a thiazoline, a benzothiazoline or a thiazolidine; a pyrimidine; a pyridine; a piperidine or pyrrolidinone; an oxazole or benzoxazole; a mercaptophenol; a thiomorpholine; a 6-mercaptopurine or a 2-thiophenomethyl amine.

5. A polymer according to claim 4 characterized in that the first functional monomer comprises phenothiazine.

6. A polymer according to claim 4 characterized in that the first functional monomer is the reaction product of phenothiazine and allyl glycidyl ether.

7. A polymer according to any of claims 1 to 6 characterized in that it comprises from 0.3 to 60 units derived from the first functional monomer per 1000 carbon atoms in the backbone polymer.

8. A polymer according to any of claims 1 to 6 characterized in that it additionally contains graft units derived from a second monomer which is an amine having a polymerizable ethylenic double bond.

9. A polymer according to claim 8 characterized in that the amine has the formula

$$\begin{array}{c} R'' \\ R - N - R' \end{array}$$

wherein R is a hydrocarbon group having a polymerizable ethylenic double bond, and R' and R", which may be the same or different, are each hydrogen, a hydrocarbon group, or a hydrocarbon group with an oxygen, sulphur or nitrogen atom as a hetero atom, or R' and R" together with the nitrogen atom to which they are attached constitute a heterocyclic ring.

10. A polymer according to claim 9 characterized in that the amine is N-vinylpyrrolidone, 1-vinylimidazole, 4-vinylpyridine or allyl amine.

11. A polymer according to any of claims 8 to 10 characterized in that it comprises from 0,1 to 60 units derived from the first functional monomer and from 0.1 to 80 units derived from the second monomer per 1000 carbon atoms in the polymer backbone.

12. A lubricating oil composition comprising a lubricating oil and additives, characterized in that said additives comprise a polymer according to any of claims 1 to 11.

13. A fuel oil comprisition comprising a fuel oil and additives characterized in that said additives comprise a polymer according to any of claims 1 to 11.

14. A method of preparing a polymer according to any of claims 1 to 7 characterized by heating the backbone polymer and the first functional monomer with a free-radical initiator ar a temperature at least as high as the decomposition temperature of the initiator.

15. A method of preparing a polymer according to any of claims 8 to 11 characterized by heating the backbone polymer and the second monomer with a free-radical initiator at a temperature at least as high as the decomposition temperature of the initiator, and subsequently heating the resulting graft polymer with the first functional monomer and the initiator at a temperature at least as high as the decomposition temperature of the initiator.

16. A method of preparing a polymer according to any of claims 8 to 11 characterized by heating the backbone polymer with the first functional monomer, the second monomer and a free-radical initiator at a temperature at least as high as the decomposition temperature of the initiator.